



Low black carbon concentration in agricultural soils of central and northern Ethiopia



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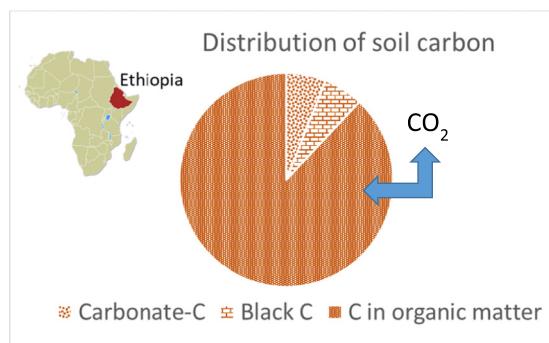
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HIGHLIGHTS

- Carbon (C) contained in soil organic matter was by far the dominant C pool, median 85%.
- This pool responded most positively to C accumulation under agroforestry and restrained grazing.
- Only 6% of total C was contained in black C.
- This distribution makes the C stocks of the studied soils very vulnerable to decomposition upon climate change.

GRAPHICAL ABSTRACT



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ABSTRACT

Soil carbon (C) represents the largest terrestrial carbon stock and is key for soil productivity. Major fractions of soil C consist of organic C, carbonates and black C. The turnover rate of black C is lower than that of organic C, and black C abundance decreases the vulnerability of soil C stock to decomposition under climate change. The aim of this study was to determine the distribution of soil C in different pools and impact of agricultural management on the abundance of different species. Soil C fractions were quantified in the topsoils (0–15 cm) of 23 sites in the tropical highlands of Ethiopia. The sites in central Ethiopia represented paired plots of agroforestry and adjacent control plots where cereal crops were traditionally grown in clayey soils. In the sandy loam and loam soils of northern Ethiopia, the pairs represented restrained grazing with adjacent control plots with free grazing, and terracing with cereal-based cropping with adjacent control plots without terracing. Soil C contained in carbonates, organic matter and black C along with total C was determined. The total C median was 1.5% (range 0.3–3.6%). The median proportion of organic C was 85% (range 53–94%), 6% (0–41%) for carbonate C and 6% (4–21%) for black C. An increase was observed in the organic C and black C fractions attributable to agroforestry and restrained grazing. The very low concentration of the relatively stable black C fraction and the dominance of organic C in these Ethiopian soils suggest vulnerability to degradation and the necessity for cultivation practices maintaining the C stock.

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1. Introduction

Soil carbon (C) is usually divided into fractions contained in 1) soil organic matter (SOM), 2) carbonates and 3) various forms of black C. Soil organic C (SOC) contained in SOM has been estimated for large geographical areas (e.g., Batjes 2002; Bradley et al. 2005; Heikkinen et al. 2013; Jones et al. 2005; Lugato et al. 2014) and even at a global scale (Batjes 1996). Inorganic C (carbonates) estimates have also been published (e.g., Batjes 1996; Rawlins et al. 2011; Shi et al. 2012). Black C is not routinely included in the estimates of soil C stocks, which globally consist of approximately 2400 Pg organic C in the top 200 cm and ca. 700 Pg of inorganic C in the top 100 cm (Batjes 1996). However, black C represents a more persistent fraction of soil C stock in comparison with SOM while also black C may be affected by management.

SOM responds to land-use practices and climate change, and its decline is recognized as one of the eight soil threats in the EU Thematic Strategy for Soil Protection (EU, 2006). According to several studies in various countries (Bellamy et al. 2008; Guo and Gifford 2002; Heikkinen et al. 2013), SOC has decreased in agricultural systems all over the world. Inorganic C in carbonates, in turn, declines upon soil acidification. By origin, black C is part of SOC, but is not considered a part of SOM for two reasons: 1) results of the Walkley-Black wet digestion method, which many soil maps on SOC and SOM are still based on, does not include this fraction (Batjes 1996) and 2) this C form is stable in soil, even for thousands of years (Atkinson et al. 2010; Lehmann et al. 2006). In this paper we chose to exclude black C from SOC, which is here defined as C contained in SOM.

Black C is formed by pyrolysis. It mainly consists of 1) charcoal, 2) biochar and 3) soot (Preston and Schmidt 2006). Charcoal occurs in soil predominantly as a consequence of forest fires, while deliberately added soil amendment is called biochar. From the chemical viewpoint, soot is similar to biochar and charcoal, even though it may contain more inorganic substances (DeLuca and Aplet 2008). Black C contributes to cation exchange capacity and water-holding capacity. Application of biochar to soil commonly increases yields (Jeffery et al. 2011; Laghari et al. 2016), however not in SOM-rich soils (Tammeorg et al. 2014). Kuhlbush and Crutzen (1995) estimated that 50–250 Tg of charcoal annually enters soil and water ecosystems. Taking into account the stability of this C form, the black C stock in soil is probably large. Even though individual studies have been conducted on the concentration or stock of black C in soil (reviewed by Preston and Schmidt 2006; Zhang et al., 2013), more measured data are needed to form accurate estimates equal to the other fractions of soil C.

Because of the assumed stability of black C, ecological research did not consider it a relevant topic of investigation until a decade ago (DeLuca and Aplet 2008). Interest was augmented by the *Terra preta* cultures of indigenous peoples of South American Indians (Glaser et al. 2000). The potential of this stable soil C fraction to counteract and resist rapid climate change has brought it to the focus of attention.

Concentration of C in Ethiopian agricultural soils is commonly at a moderate level at the very least, compared to many other tropical countries. For example, Sillanpää (1982) measured an average SOC content of 2.2% in 71 agricultural soils of Ethiopia, while the mean for 574 soil samples from six other African countries was only 1.3%. This result may partly be connected to the high clay content (45%) of Sillanpää's Ethiopian soils compared to the rest of the sampled African soils (22%). Shifting cultivation is still a common agricultural practice throughout the tropical world, and burning of the vegetation results in a substantial input of black C into the soil (Kuhlbush and Crutzen 1995; Rumpel et al. 2006). The area of natural forests in Ethiopia has declined from approximately 40% to <3% in 100 years, part of it being subjected to fire (Berhaun, 2005). Wood and charcoal are extensively used as fuel throughout Africa, and the remaining ash and charcoal pieces are often spread in fields or in the soil of kitchen middens. Ethiopian soils may therefore be high in black C.

In this study we investigated the distribution of black C, SOC and carbonates in agricultural soils in two areas in Ethiopia. Conventional cereal production was practiced in the sampled fields, and agroforestry, terracing and restrained grazing were practiced as improved management regimes. In our earlier study (Rimhanen et al. 2016) it was found that agroforestry and restrained grazing increased total C in soil. Now the objective was to obtain quantitative information concerning the fractions of C, particularly of black C to advance understanding of the persistence of soil C stocks. We hypothesized that there is a substantial pool of black C in our experimental soils and the concentration of black C remains unchanged and gains of soil C appear solely in the more labile organic C pool.

2. Material and methods

The soil material in our study originated from Sire (mean elevation 1970 m asl, mean precipitation 868 mm, mean temperature 15–20 °C) in the Oromia region of the Central Rift Valley, Ethiopia, and in Kobo (1590 m asl, 631 mm, 21–25 °C) in the Amhara region, northern Ethiopia (Fig. 1), both representing important food-producing areas. Field plots with soil conservation and adjacent plots with traditional practices were sampled. The soil conservation practices represented in our study were farmland terracing and areas with restrained grazing in Kobo and agroforestry around the homesteads in Sire. Traditional "highland temperate mixed" farming (Dixon et al. 2001) was represented by cereal and lentil cultivation adjacent to terracing and agroforestry plots, and by grazing land adjacent to areas with restrained grazing where domestic animals were excluded. The median (and range) duration for the improved management was 8.5 (6–20) years for agroforestry, 13 (6–17) years for restrained grazing and 7 (5–10) years for terraced plots. The study areas, agricultural practices, sampling and general soil properties have been described in detail in our previous study (Rimhanen et al. 2016), where total C concentrations and stocks were investigated. Briefly, soil (0–15 cm) was sampled from seven restrained grazing sites, eight terraced and agroforestry sites and from adjacent control plots for each study site. Three independent replicates, consisting of ten sub-samples, were collected from each plot with an auger. The Kobo area was dominated by loam and sandy loam soils, with 14%

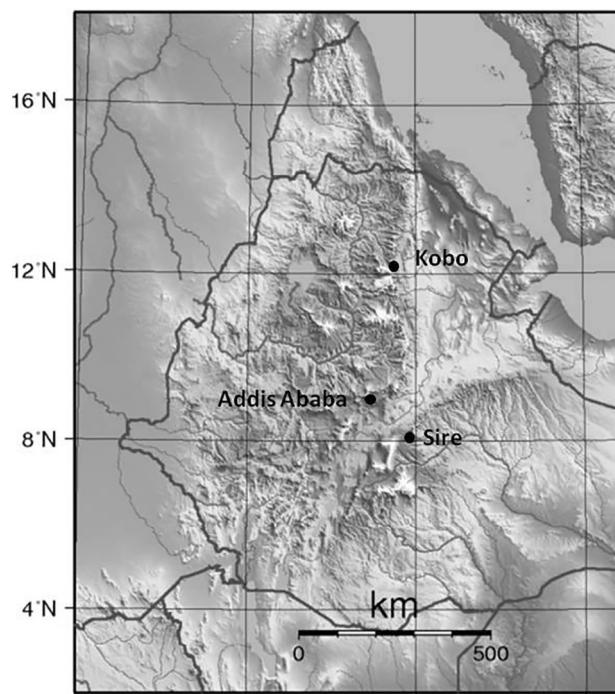


Fig. 1. Locations of the sampling areas of Sire and Kobo in central and northern Ethiopia.

clay and 58% sand contents on average, and as much as 12% of coarse fragments, expressed on the volumetric basis. In Sire, the soil texture ranged from clay to clay loam, the average clay and sand contents being 39% and 24%, respectively, with only 3% of coarse fragments. The average pH (1:2.5 soil: water) of both areas was 7.8, with all results falling within the range of 7.4–8.2. The bulk densities, needed for calculating the C stocks and determined with a core method, ranged from 0.97 to 1.50 kg dm⁻², with a mean of 1.25 kg dm⁻².

2.1. Determination of soil carbon

Total C of the fine earth fraction (<2 mm) of all soil samples was analysed by dry combustion at 1100 °C with a Leco CN-2000 analyser (Leco Corporation, MI, USA) or a VarioMAX CN-analyser (Elementar Analysensysteme GmbH) using 500-mg soil samples. Carbon contained in the carbonates was determined indirectly by digesting 3-g soil samples with 5 ml of 6 M HCl for 30 min (Ellert and Rock 2007). Thereafter the mixture was transferred on a filter paper (Whatman Blue Ribbon 589/3) and washed five times with deionized water to avoid the possible corrosion of metal surfaces by acidic vapours during the further experimental steps. Dried soil samples (60 °C, 24 h) were analysed for total C, and the difference between untreated soil and HCl-treated soil was taken as the measure of carbonate C. Black C and SOC were determined with the fractionation method of Kurth et al. (2006), developed for measuring charcoal in forest soils. In this method, carbonates and SOM are removed from the sample, and the total C remaining in the sample is assumed to be black C. Briefly, a 3-g soil sample was digested with 30 ml of 1 M HNO₃ and 60 ml of concentrated H₂O₂ at room temperature for 30 min. The mixture was boiled slowly for 16 h, divided into two consecutive days. The samples were dried (60 °C, 24 h), ground and analysed for total C, assumed to represent black C. Quartz sand was used as the blank. An estimate for SOC was obtained by subtracting the concentrations of carbonate C and black C from the total C of the untreated sample.

The fractionation method was tested in four soil samples (Table 1) from Finland by measuring the recovery of biochar added into the soil. The biochar was manufactured by Tammeorg et al. (2014) from spruce (*Picea abies*) that was pyrolyzed for 10–15 min at 550–600 °C. C content of the biochar material was 81.3%, and 5.5% of C was contained in carbonates. The biochar additions were 0, 4 and 8 g of biochar material into 400-g samples of air-dry soil (three replicates), corresponding to 0, 30 and 60 t ha⁻¹ in a 25-cm plough layer. The soil-biochar mixtures were incubated at a moisture of 20% (sand) or 25% (clay) for 30 days at 5 °C. Dried soil samples were analysed for the fractions of C as presented above in three replicates. Total C of the unamended soil samples ranged from 0.8% to 3.4%. While SOC clearly dominated in the topsoils, all test soil samples had a substantial concentration of black C (0.3–0.6%). Addition of biochar elevated total C (Fig. 2 for sand, results of clay not presented in detail). As a response to the carbonates contained in the biochar material, some increase in carbonate C fraction was observed in all soil samples but no change was observed in the SOC fraction. The most remarkable change after biochar addition was measured in the black C fraction. In the sandy soil, 90% of C contained in the added biochar was recovered during the fractionation but on average 63% was recovered from the clay soil. These results indicate that the fractionation method is able to quantify different C pools at least

satisfactorily. The average coefficients of variation (CV), calculated based on the replicates, were 5.2%, 9.0% and 12.8% for total C, SOC and black C, respectively, while the CV for the small carbonate fraction was 34%.

2.2. Data analysis

The statistical analysis of the soil C concentrations (SOC, black C and their proportions of total C) were based on generalized linear mixed models for a split-plot design, where the three groups of plot pairs (agroforestry, areas of restrained grazing and farmland terracing) were the levels of the whole-plot factor and the two management practices (traditional and improved) were the levels of the sub-plot factor. The models included three fixed effects (main effects of the whole-plot factor and the sub-plot factor and their interaction) and two random effects (whole-plot error and sub-plot error). The means of ten subsamples were used as observations in the statistical analyses.

The charcoal concentrations were normally distributed, but the distributions of other dependent variables were skewed. Generalized linear mixed models with beta (SOC %) and gamma (SOC and black C %) distributions were used in the analysis to satisfy the assumptions of the models (Gbur et al. 2012). Black C was fitted by using the restricted maximum likelihood (REML) estimation method and others by applying the residual pseudo-likelihood with a subject-specific expansion (RSPL). Degrees of freedom were calculated using the Kenward-Roger method. The normality of residuals was checked using box plots (Tukey 1977). The residuals were also plotted against the fitted values. These plots indicated that the assumptions of the models were adequate. Comparison of the means was performed using two-tailed *t*-tests. The analyses were performed using the GLIMMIX procedure in version 9.3 of the SAS/STAT software (Littell 2006).

3. Results

The CVs, based on three independent replicates of each plot, indicated that the sampled plots were reasonably homogeneous, except for the small fraction of carbonates. For total C, SOC and black C, the average CVs were 10, 12 and 10%, respectively, but 49% for C in carbonates.

The clayey soils of Sire, central Ethiopia, contained more total C (mean 2.4%, median 2.2%) than the drier and more coarse-textured soils of Kobo in northern Ethiopia (mean 1.0%, median 1.1%). The terraced fields and their traditionally cultivated control plots in particular were lower in C (mean 0.74%) than the adjacent plots with restrained grazing (mean 1.4%). The results of total C and their relationship to cultivation practices have been presented and discussed in detail by Rimhanen et al. (2016).

SOC was by far the dominating C fraction, with a median of 85% and a range of 53–94% of total C. Despite the rather high pH, the soils were practically non-calcareous, with a carbonate C range of 0–0.86% and a mean of 0.08%. The mean corresponded to 0.7% and the maximum to 7% calcite, while calcareous soils by definition contain at least 15% calcite. The carbonate C median was as low as 0.07%, representing 6% of total C, with a range of 0–41%. Within the narrow range of carbonate concentrations and soil pH (7.4–8.3), no correlation was observed between carbonate content and soil pH. Although the highest concentrations occurred in soils with pH > 8, soils of similar pH with very low carbonate C concentrations were also observed.

Black C concentrations ranged from 0.03 to 0.24% of soil mass, with one outlier in Kobo that had a concentration of 0.31%, while the concentration median was 0.10%. Only 6% of total C was contained in black C, with a range of 4–21%. Black C comprised 10–15% of total C in four of the terraces and their control plots that were very low in total C (0.4–0.9%) despite average-level concentrations (ca. 0.07%) of black C, while all other results were 4–9% of total C. Despite the narrow range of black C, Fig. 3 indicates that there was a close linear relationship between SOC and black C concentrations.

Table 1
Characteristics of the soil samples used for testing the fractionation method for C.

Characteristic	Clay 0–20 cm	Clay 30–50 cm	Sand 0–20 cm	Sand 30–50 cm
Texture	Sandy clay loam	Clay	Sand	Sand
Clay %	24	46	4	2
Silt %	34	39	16	5
Sand %	42	15	80	93
pH(H ₂ O)	6.4	5.9	5.8	6.2

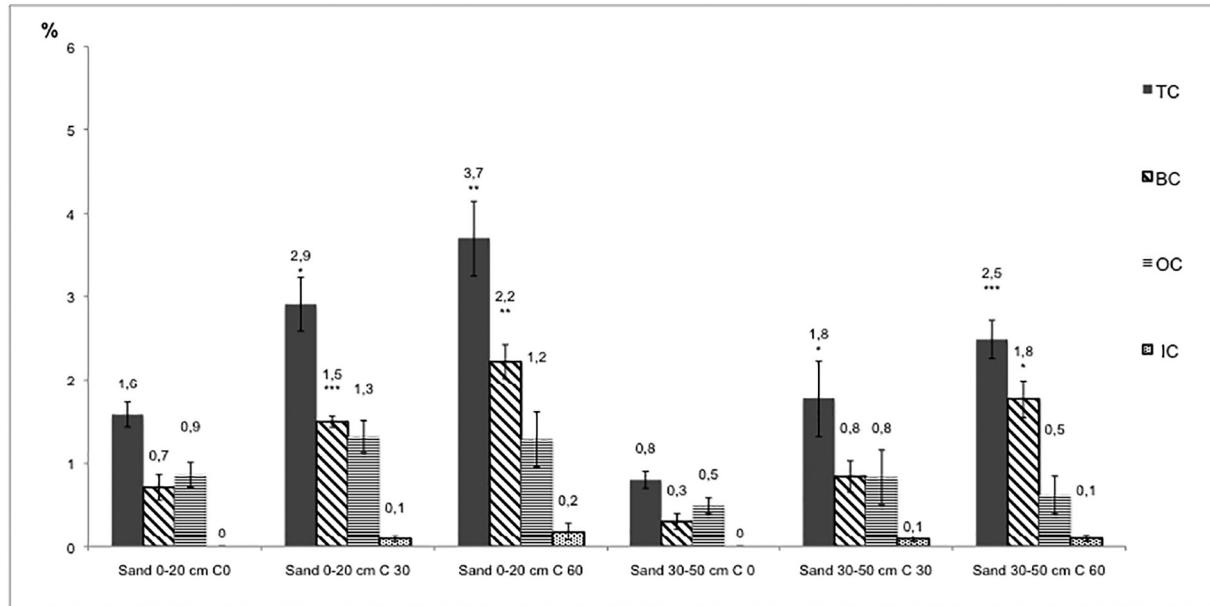


Fig. 2. Carbon (C) contents in the sandy topsoil (0–20 cm) and subsoil (30–50 cm) at three rates of added biochar: C0 = 0 t ha⁻¹ (control), C30 = 30 t ha⁻¹ and C60 = 60 t ha⁻¹. TC = total C, BC = charcoal/biochar, OC = C in organic matter, IC = C contained in carbonates. The standard deviations are presented as error bars. Statistical significance of the differences in TC, BC and IC compared to the control: *** $p=0.001$, ** $p=0.01$, * $p=0.05$.

Among the soil conservation practices, the plots for restrained grazing and agroforestry had statistically significantly higher concentrations of SOC and black C than the control plots (Table 2). The concentrations of carbonate C were not affected by the treatments.

Using the fixed depth approach, the stocks of the different C pools were calculated for the top 15 cm of soil, corresponding to the sampling depth. The mean stock of black C in the loam and sandy loam soils of Kobo was 1.2 t ha⁻¹. This stock was quite independent of the treatments (restrained grazing, terracing, traditional cereal cultivation) and, compared to the control, was only 0.2 t ha⁻¹ higher in the fields where restrained grazing was practised while C contained in SOM was increased from 13 t ha⁻¹ by 4.5 t ha⁻¹. In the clay and clay loam soils of Sire the mean stock of black C in the traditionally cultivated soils was 2.8 t/ha and 0.7 t ha⁻¹ higher in the agroforestry plots. The improved management mostly influenced the SOC pool which amounted to 36.4 t ha⁻¹ in the control plots and was 9.3 t ha⁻¹ higher in the agroforestry plots.

4. Discussion

Agroforestry and restrained grazing increase the input of plant residues into the soil and elevate the concentration of soil C (Rimhanen et al. 2016). The present results show that most of the increase by far took place in the SOC fraction but there was also a statistically significant increase in the fraction of supposedly black C. According to the interviews, no marked fires occurred in the studied areas during the improved practices (Rimhanen et al. 2016). There are two alternative causes for the measured increase in black C. First, ash mixed with charcoal may have been used as a fertilizer in the improved practices. Second, and more likely, because the outcome was uniform, part of the litter had been incorporated into forms that were too recalcitrant or not accessible for oxidation by the HNO₃-H₂O₂ treatment. Kurth et al. (2006) mentioned that digestion effectively removed most organic C. This conclusion is also supported by the high linear correlation between the fractions of SOC and black C. Therefore C remaining in soil after the HNO₃-H₂O₂ -digestion, besides black C, may contain SOC forms that are chemically most stable or physically protected. Even though this fraction may not be purely black C, it likely represents the soil C pool that is most resistant against oxidation and which may thus form a buffer against the decline of SOC. Terracing contributes to decreased erosion and may thereby result in more C remaining in the field. Since terracing itself does not increase C inputs into the soil, no statistically significant changes in C fractions were observed.

Our results did not support the hypothesis that soils of northern and central Ethiopia are high in black C. On the contrary, on an average only 6% of soil C was found in the fraction resistant against the HNO₃ - H₂O₂ oxidation. This black C content is much lower than reported in studies of cooler climates. According to Kurth et al. (2006), black C in five agricultural topsoils of northern USA had a range 0.29–0.92%, representing an average 17% of total C and in another five US soils, black C represented 10–35% of total C (Skjemstad et al. 2002), and in Australia black C amounted up to 40% of total C (Skjemstad et al. 1996). However, our results of black C correspond to other areas of warm climates. In the <2-mm fraction of two sandy savannah soils in Zimbabwe (Bird et al.

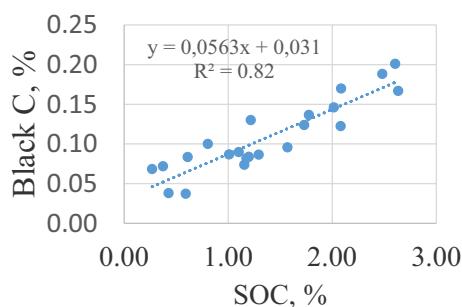


Fig. 3. The relationship between the SOC, i.e., C contained in SOM, and black C concentrations in the sampled plots in Ethiopia. SOC = soil organic carbon; SOM = soil organic matter; C = carbon.

Table 2

Test results for the comparison of the soil conservation (cons) and traditional (trad) management practices in terms of SOC (C contained in soil organic matter) and black C. The results are presented without one discrepant value for the traditional control in a pair of farmland terracing. N = number of plots.

Management practice	N	SOC, %			Black C, %		
		Mean and 95% CI ^b in trad	Difference (cons-trad) ^a	p-Value			
Agroforestry (Sire)	16	1.74 1.34–2.25	0.55	0.028*	0.14 0.12–0.16	0.04	0.013*
Restrained grazing (Kobo)	14	0.98 0.75–1.30	0.66	0.001***	0.07 0.05–0.10	0.04	0.019*
Terracing (Kobo)	15	0.49 0.38–0.64	0.13	0.066 ^{ns}	0.06 0.04–0.09	0.01	0.72 ^{ns}

^a The estimated means for improved and traditional management practices are presented in the original scale and the difference between the resulting values was calculated. The differences were tested on the link scale using two-tailed t-tests.

^b 95% confidence intervals (CIs) for the means.

* p = 0.001.

** p = 0.05. n.s. p>0.05.

1999), “oxidation-resistant elemental C (OREC)” stood for 3.6 and 2.2% of SOC, or 0.6 and 1.0% of soil dry weight. In six surface horizons of agricultural soils of Laos (Rumpel et al. 2006), OREC constituted 5.5–7.3% of SOC, or 1.2–2.7% of soil. In a large material of 260 soil samples from the Chinese loess plateau (Zhan et al., 2013), black C concentration averaged at 0.07%, and in agreement with our results, was higher in clayey soils than in coarse-textured soils.

5. Conclusions

Most C accumulated in the soil during the application of agroforestry and restrained grazing was contained in SOM oxidized by a HNO₃ - H₂O₂ treatment. Minor increases of more resistant forms of C were also measured. As most C in Ethiopian soils is contained in SOC, these soils are likely very susceptible to the adverse effects of organic matter decline. Therefore sustainable use of these soils strongly calls upon practices that contribute to the maintenance and continuous build-up of soil organic matter.

Author contributions

K.R. and H.K. selected the management practices and study sites. K.R. collected the samples and organized the data. J.M. carried out the experiment on biochar recovery. H.K. supervised the study regarding the Sire and Kobo soils and M.Y·H the biochar recovery study. J.K. designed and performed the data analyses. All authors contributed to the study design and to writing the manuscript.

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References

- Atkinson, C., Fitzgerald, J., Hipps, N., 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. *Plant Soil* 337, 1–18.
- Batjes, N.H., 1996. Total carbon and nitrogen in soils of the world. *Eur. J. Soil Sci.* 47, 151–163.
- Batjes, N.H., 2002. Carbon and nitrogen stocks in the soils of Central and Eastern Europe. *Soil Use Manag.* 18, 324–329.
- Bellamy, P.H., Loveland, P.J., Bradley, R.I., Lark, R.M., Kirk, G.J.D., 2008. Carbon losses from all soils across England and Wales 1978–2003. *Nature* 437, 245–248.
- Berhanu, L., 2005. Global Forest Resources Assessment 2005, Ethiopia Country Report 036. FAO, Rome.
- Bird, M.I., Moyo, C., Veenendaal, E.M., Lloyd, J., Frost, P., 1999. Stability of elemental carbon in a savanna soil. *Glob. Biogeochem. Cycles* 13, 923–932.
- Bradley, R.I., Milne, R., Bell, J., Lilly, A., Jordan, C., Higgins, A., 2005. A soil carbon and land use database for the United Kingdom. *Soil Use Manag.* 21, 363–369.
- DeLuca, T.H., Aplet, G.H., 2008. Charcoal and carbon storage in forest soils of the Rocky Mountain West. *Forest Ecol. Environ.* 6, 18–24.
- Dixon, J.A., Gibon, D.P., Gulliver, A., 2001. *Farming Systems and Poverty: Improving Farmers' Livelihoods in a Changing World*. FAO, Rome.
- Ellert, B.H., Rock, L., 2007. Stable isotopes in soil and environmental research. In: Gregorich, E.G., Carter, M.R. (Eds.), *Soil Sampling and Methods of Analysis*, 2nd Ed. CRC Press, Boca Raton, FL, USA, pp. 693–711.
- EU, 2006. Communication from the commission to the council, the European Parliament, the European economic and social committee and the Committee of the Regions – thematic strategy for soil protection. *Commentary 2006 (231)* (final, 12 pp. accessed 22 April, 2014).
- Gbur, E., Stroup, W.W., McCarter, K.S., et al., 2012. *Analysis of Generalized Linear Mixed Models in the Agricultural and Natural Resources Sciences*. American Society of Agronomy, Madison.
- Glaser, B., Balashov, W., Haumaier, L., Guggenberger, G., Zech, W., 2000. Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region. *Org. Geochem.* 31, 669–678.
- Guo, L.B., Gifford, R.M., 2002. Soil carbon stocks and land use change: a meta analysis. *Glob. Chang. Biol.* 8, 345–360.
- Heikkilä, J., Ketoja, E., Nuutinen, V., Regina, K., 2013. Declining trend of carbon in Finnish cropland soils in 1974–2009. *Glob. Chang. Biol.* 19, 1456–1469.
- Jeffery, S., Verheijen, F.G.A., van der Velde, M., Bastos, A.C., 2011. A quantitative review of effects of biochar application to soils on crop productivity using meta-analysis. *Agric. Ecosyst. Environ.* 144, 175–187.
- Jones, R.J.A., Hiederer, R., Rusco, E., Montanarella, L., 2005. Estimating organic carbon in the soils of Europe for policy support. *Eur. J. Soil Sci.* 56, 655–671.
- Kuhlbusch, T.A.J., Crutzen, P.J., 1995. Towards a global estimate of black carbon residues of vegetation fires representing a sink to atmospheric CO₂ and a source of O₂. *Glob. Biogeochem. Cycles* 9, 491–501.
- Kurth, V.J., MacKenzie, M.D., DeLuca, T.H., 2006. Estimating charcoal content in forest mineral soils. *Geoderma* 137, 135–139.
- Laghari, M., Naidu, R., Xiao, B., Hu, Z., Mirjat, M.S., Hu, M., Kandhro, M.N., Chen, Z., Guo, D., Jogi, Q., Abudi, Z.N., Fazal, S., 2016. Recent developments in biochar as an effective tool for agricultural soil management: a review. *J. Sci. Food Agric.* 96, 4840–4849.
- Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems – a review. *Mitig. Adapt. Strateg. Glob. Chang.* 11, 403–427.
- Littell, R.C., 2006. *SAS for Mixed Models*. SAS Institute (814 pp).
- Lugato, E., Panagos, P., Bampa, F., Jones, A., Montanarella, L., 2014. A new baseline of organic carbon stock in European agricultural soils using a modelling approach. *Glob. Chang. Biol.* 20, 313–326.
- Preston, C.M., Schmidt, M.W.I., 2006. Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences* 3, 397–420.
- Rawlins, B.G., Henrys, P., Breward, N., Robinson, D.A., Keith, A.M., Garcia-Bajo, M., 2011. The importance of inorganic carbon in soil carbon databases and stock estimates: a case study from England. *Soil Use Manag.* 27, 312–320.
- Rimhanen, K., Ketoja, E., Yli-Halla, M., Kahiluoto, H., 2016. Carbon sequestration in Ethiopian agriculture has more potential than previously estimated. *Glob. Chang. Biol.* 22, 3739–3749.
- Rumpel, C., Alexis, M., Chabbi, A., Chaplot, V., Rasse, D.P., Valentini, C., Mariotti, A., 2006. Black carbon contribution to soil organic matter in tropical sloping land under slash and burn agriculture. *Geoderma* 130, 35–46.
- Shi, Y., Baumann, F., Ma, Y., Song, C., Kühn, P., Scholten, T., He, J.-S., 2012. Organic and inorganic carbon in the topsoil of the Mongolian and Tibetan grasslands: pattern, control and implications. *Biogeosciences* 9, 2287–2299.

- Sillanpää, M., 1982. Micronutrients and the nutrient status of soils: a global study. FAO Soils Bull. 48 (FAO, Rome, 444 pp).
- Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., McClure, S.G., 1996. The chemistry and nature of protected carbon in soil. *Aust. J. Soil Res.* 34, 251–271.
- Skjemstad, J.O., Reicosky, D.C., Wilts, A.R., McGowan, J.A., 2002. Charcoal carbon in U.S. agricultural soils. *Soil Sci. Soc. Am. J.* 66, 1249–1255.
- Tammeorg, P., Simojoki, A., Mäkelä, P., Stoddard, F., Alakukku, L., Helenius, J., 2014. Short-term effects of biochar on soil properties and wheat yield formation with meat bone meal and inorganic fertiliser on a boreal loamy sand. *Agric. Ecosyst. Environ.* 191, 108–116.
- Tukey, J.W., 1977. *Exploratory Data Analysis*. Addison-Wesley, Reading, UK (688 pp).
- Zhang, C., Cao, J., Han, Y., Huang, S., Tu, X., Wang, P., An, Z., 2013. Spatial distributions and sequestrations of organic carbon and black carbon in soils from the Chinese loess plateau. *Sci. Total Environ.* 465, 255–266.